



## **Procedures for determination of $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , $^{237}\text{Np}$ , $^{234,238}\text{U}$ , $^{228,230,232}\text{Th}$ , $^{99}\text{Tc}$ and $^{210}\text{Pb}$ - $^{210}\text{Po}$ in environmental materials**

**Chen, Q.J.; Aarkrog, Asker; Nielsen, Sven Poul; Dahlgaard, Henning; Lind, B.; Kolstad, A.K.; Yu, Yixuan**

*Publication date:*  
2001

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

### *Citation (APA):*

Chen, Q. J., Aarkrog, A., Nielsen, S. P., Dahlgaard, H., Lind, B., Kolstad, A. K., & Yu, Y. (2001). Procedures for determination of  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{237}\text{Np}$ ,  $^{234,238}\text{U}$ ,  $^{228,230,232}\text{Th}$ ,  $^{99}\text{Tc}$  and  $^{210}\text{Pb}$ - $^{210}\text{Po}$  in environmental materials. Risø National Laboratory. Denmark. Forskningscenter Risø. Risø-R No. 1263(EN)

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# **Procedures for Determination of $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , $^{237}\text{Np}$ , $^{234,238}\text{U}$ , $^{228,230,232}\text{Th}$ , $^{99}\text{Tc}$ and $^{210}\text{Pb}$ - $^{210}\text{Po}$ in Environmental Materials**

**Qingjiang Chen, Asker Aarkrog, Sven P. Nielsen, Henning  
Dahlgaard, Bjørn Lind\*, A.K. Kolstad\* and Yixuan Yu**

**\* Norwegian Radiation Protection Authority, Norway**

ISBN 87-550-2871-3  
ISBN 87-550-2966-3 (Internet)  
ISSN 0106-2840

Print: Pitney Bowes Management Services Denmark A/S, 2001

# Contents

Preface 4

Determination of plutonium in 200 liters sea water 4

Plutonium procedure for 200 liters seawater 5

Plutonium procedure for 10 g sediment or soil 7

Plutonium procedure for fish, mussel and other biological samples 8

Plutonium procedure for seaweed 9

Plutonium procedure for 1-2 g sediment or soil 10

Americium procedure for 10 g sediment, soil and 200 liters seawater 11

Neptunium ( $^{237}\text{Np}$ ) procedure for 10 g sediment, soil and seawater 12

Neptunium procedure for sediment and soil 13

Neptunium ( $^{237}\text{Np}$ ) procedure for 100 liters seawater 15

Procedure for simultaneous determination of  $^{237}\text{Np}$  and  $^{239,240}\text{Pu}$  in 10 g sediment or soil 15

Procedure for simultaneous determination of  $^{239,240}\text{Pu}$  and  $^{237}\text{Np}$  in 200 liters seawater 17

Determination of uranium in soil and sediment 18

Determination of uranium in food products 20

Determination of thorium in soil and sediment 21

Determination of thorium in food products 22

Determination of  $^{99}\text{Tc}$  in 50 liters seawater 23

Technetium-99 procedure for 200 liters seawater 24

Technetium ( $^{99}\text{Tc}$ ) procedure for seaweed-A new method 25

Determination of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in mussel, fish, sediment and petroleum 27

References 30

# Preface

*Since 1987, the Department of Nuclear Safety Research, Risø National Laboratory has developed procedures for analysis of low-level amounts of radioactivity in large samples of 200 liters seawater, 10 gram sediment, soil and other environmental materials. These analytical procedures provide high chemical yields, good resolution and excellent decontamination factors for large environmental samples analysed by alpha spectrometry and mass spectrometry (ICPMS). The procedure have been checked through practical analysis work and are used in Norway, the Netherlands, Germany, Spain, France and Denmark.*

## Determination of plutonium in 200 liters sea water

### Abstract

A procedure for the determination of plutonium in seawater is described. The plutonium is pre-concentrated by scavenging with  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ . This purifies for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and amphoteric elements.

The method is based on a new procedure in which the principle of controlled valence is applied. The redox system  $\text{SO}_3^{2-} / \text{NO}_2^-$  was used <sup>(1)</sup> first to reduce to  $\text{Pu}^{3+}$  and afterwards to oxidize to  $\text{Pu}^{4+}$ . The  $\text{Pu}^{3+}$  is separated from U and  $^{210}\text{Po}$  by solvent extraction with TIOA – 6-10 M HCl. Followed by anion exchange of  $\text{Pu}^{4+}$  in 8 M  $\text{HNO}_3$ .

The decontamination factors of the procedure are  $>1.7 \cdot 10^6$  for U and  $>6.3 \cdot 10^4$  for Th. The chemical yield is 70-85%.

### Principle

Higher valences of plutonium are rapidly reduced to  $\text{Pu}^{3+}$  by  $\text{K}_2\text{S}_2\text{O}_5$  in 200 liter seawater at pH=2.  $\text{Pu}(\text{OH})_3$  and transuranium elements are precipitated by  $\text{Fe}(\text{OH})_2$ - $\text{Fe}(\text{OH})_3$  at pH=10. The hydroxide precipitation is repeated twice, the first time to remove a large amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at pH=8-10 in a  $\text{NH}_3$  system and the second time to separate the amphoteric elements in a 0.3-0.5 M NaOH solution. In order to get rid of the large amount of sulfur from sulfite (especial in sediment), the sample solution is boiled with  $\text{H}_2\text{O}_2$  in 1 M HCl. The reaction is  $\text{S} + 2 \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$ .

The  $\text{H}_2\text{SO}_3$  is decomposed to  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , which is evaporated, or the  $\text{H}_2\text{SO}_3$  is further oxidized to  $\text{H}_2\text{SO}_4$ .

The control of valence of plutonium plays an important role in the procedure. Plutonium is reduced to  $\text{Pu}^{3+}$  by  $\text{K}_2\text{S}_2\text{O}_5$  and carried by  $\text{Fe}(\text{OH})_2$  which is dissolved in 6 M HCl. The  $\text{UO}_2\text{Cl}_4^{2-}$ ,  $\text{NpCl}_6^{2-}$  and  $\text{PoCl}_6^{2-}$  are extracted into 10%TIOA/xylene.  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Th}^{4+}$  are in the aquatic phase, which is evaporated to about 0.5-1 mL. The sample is diluted to 20 mL 0.5 M HCl. The plutonium is reduced to  $\text{Pu}^{3+}$  by adding  $\text{K}_2\text{S}_2\text{O}_5$ . Then  $\text{Pu}^{3+}$  is rapidly oxidized to

$\text{Pu}^{4+}$  by  $\text{NaNO}_2$  and kept in this oxidation state. The  $\text{Pu}(\text{NO}_3)_6^{2-}$  and  $\text{Th}(\text{NO}_3)_6^{2-}$  are absorbed on an AG1-X<sub>4</sub> ion exchange column and the  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  are passed through the column in 8 M  $\text{HNO}_3$ . (This elute is kept for later Am determination). The column is finally washed with 8 M  $\text{HNO}_3$  to get rid of the uranium and with 12 M  $\text{HCl}$  in order to separate the thorium.

To avoid plutonium micro absorption on the column wall and on other surfaces, sodium salts are used in every step of the procedure. As yield tracer  $^{242}\text{Pu}$  is used.

## Plutonium procedure for 200 liters seawater

### On board the ship

- 1) Acidify 200 liters seawater to pH=2 with 200 mL 12 M  $\text{HCl}$ . Add 2 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$  and 100 g  $\text{K}_2\text{S}_2\text{O}_5$ . Stir by bubbling for 1 h to reduce all Pu valences to  $\text{Pu}^{3+}$ .
- 2) Basify the 200 liters seawater to pH about =10 with diluted  $\text{NaOH}$  (0.5-1 M) to precipitate  $\text{Fe}(\text{OH})_2$ - $\text{Pu}(\text{OH})_3$ - $\text{Am}(\text{OH})_3$ . The dilute  $\text{NaOH}$  is added to reduce the formation of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . Let stay for 5 h or overnight. Siphon off the supernatant liquid to get about 5 liters of  $\text{Fe}(\text{OH})_2$  slurry.
- 3) Acidify the sample to about 0.1 M  $\text{HCl}$  with concentrated  $\text{HCl}$  (about 15 mL/liter) Transfer the sample to laboratory for analysis.

### In the laboratory

- 4) Slowly add 6%  $\text{NH}_3$  to pH=9-10. Let stay for 4 h. Pour out the supernatant liquid. Filter the precipitate on GF/A filter paper under suction.
- 5) The precipitate is dissolved in 50 mL 12 M  $\text{HCl}$  + 50 mL 14.4 M  $\text{HNO}_3$  in a 400 mL beaker. Cover the beaker with a glass disc and heat for 1-2 h to digest the sample.
- 6) Evaporate to about 30 mL and transfer the solution to 250 mL centrifuge tube. Add  $\text{NH}_4\text{OH}$  to pH about 8-9. Centrifuge, Pour the supernatant to remove the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .
- 7) The precipitate is dissolved in 5-10 mL 12 M  $\text{HCl}$ . Dilute the solution to 160 mL with water. Add 150 mg  $\text{K}_2\text{S}_2\text{O}_5$ . Stir and let stay for 20 min. Add  $\text{NaOH}$  to pH=10, centrifuge, and pour the supernatant.
- 8) The precipitate is dissolved in 20 mL 12 M  $\text{HCl}$  and 20 mL 6 M  $\text{HCl}$ . The concentration of  $\text{HCl}$  is about 6 M. Transfer the solution to a 250 mL separator. Extract with 80 mL 10%  $\text{TIOA}$ /xylene. Shake 5 min. Discard the or-

ganic phase (containing U, Po and Fe). Filter the aquatic phase to the centrifuge tube. Add 10 mg  $\text{Fe}^{+3}$  and  $\text{NH}_3$  to pH=10. Centrifuge and pour the supernatant.

- 9) The sample is dissolved in 5 ml 12 M HCl and dilute to 170 mL. Add 0.5 g  $\text{K}_2\text{S}_2\text{O}_5$  to sample and stir for 20 min. Add NaOH to pH=10, centrifuge, pour the supernatant.
- 10) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2-3 mL 12 M HCl and measure the volume of solution. Add 50 mg  $\text{NaNO}_2$ . Acidify the to 8 M  $\text{HNO}_3$  with 14 M  $\text{HNO}_3$  ( $V_s / V_{\text{HNO}_3} = 1 / 1.3$ ).
- 11) The solution is passed through an anion ion exchange column (13 x 1cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1,5mL/min.
- 12) Wash the column with 20 mL 8 M  $\text{HNO}_3$  (Combine the passed solution and the 20 mL washing solution for americium analysis.). \*Wash the column with 70 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl. The flow rate is about 1 mL/min.
- 13) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  + 0.1 g NaCl.
- 14) Add 4 mL 14 M  $\text{HNO}_3$  and evaporate to dryness.
- 15) 15) The sample is dissolved in 6 mL 6 M HCl. Transfer the solution to 250 mL centrifuge tube. Wash the beaker and combine the solution to the tube. Dilute to 170 mL. Add 200  $\text{K}_2\text{S}_2\text{O}_5$ , 30 mg  $\text{Fe}^{3+}$  and stir for 20 min. Add NaOH to pH=10, centrifuge and pour the supernatant.
- 16) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2 mL 12 M HCl and dilute to 10 mL with water. Add 13 mL 14.4 M  $\text{HNO}_3$  to 8 M  $\text{HNO}_3$ .
- 17) Repeat the steps 11).
- 18) Wash the column with 80 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl.
- 19) \*\* Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  + 0.6 g NaCl.

### Electrodeposition

- 20) Add 4 mL 14 M  $\text{HNO}_3$  and 0.3 mL 18 M  $\text{H}_2\text{SO}_4$ . Evaporate to dryness on 150°C overnight. Heat at 400°C for 40 minutes.
- 21) Dissolve the sample in 7 mL 0.05 M  $\text{H}_2\text{SO}_4$ . Wash the beaker 3 times, each time with 3 mL 0.05 M  $\text{H}_2\text{SO}_4$ . Transfer the solutions to a electrodeposition cell \*\*\*. Add 2 drops of methylblue and 25%  $\text{NH}_3$  to pH=2.5. Electrodeposit for 4-5 hours. The current is 0.7A/cm<sup>2</sup>. Cool the cell with water. Add 0.5 mL 25%  $\text{NH}_3$  to the cell and let stay for 30 seconds. Switch off the current.
- 22) Dismantle the disc from the cell. Hold the disc with tweezers. Dip the disc into water pH=9 ( $\text{NH}_3$ ) 2 times, each time for 2 seconds. The water on the

disc surface is sucked with soft paper. Put the disc in a 90°C heating cabinet for 15 min and the sample is ready for  $\alpha$ -measurement.

---

\* Wash the column with 8 M HNO<sub>3</sub> and 12 M HCl: In order to increase the efficiency of cleaning and to avoid surface contamination of the glass wall of the column, the solution is added 10 mL by 10 mL. The surface of the column should dry before the next 10 mL is added.

\*\*Strip with 70 mL 2 M HCl + 2 g NH<sub>2</sub>OH·HCl. Add 4 mL 14 M HNO<sub>3</sub> to the stripped solution and evaporate to dryness. Add 5 mL 14.4 M HNO<sub>3</sub> and evaporate to dryness. The sample is dissolved in 4% HNO<sub>3</sub> for ICPMS measurement.

\*\*\*Preparation of the hydrophilic surface of a disc: The disc is fixed to an electrodeposition cell which is checked for leaks. Clean the cell and disc with washing powder solution and polish the surface of the disc with cotton which is held by tweezers. Wash the cell with distilled water for 10 times. The surface of the disc becomes hydrophilic which is good for electrodeposition. If the disc is washed with alcohol or acetone, the surface of the disc becomes hydrophobic, which is bad for electrodeposition.

## Plutonium procedure for 10 g sediment or soil

- 1) Transfer 10g homogenized soil or sediment into a beaker. Burn at 550°C over night.
- 2) Add Am-243 and Pu-242 tracer, (0.2 g FeCl<sub>3</sub> · 6 H<sub>2</sub>O for sand sample) and 40 mL aqua regia. Cover with glass disk. Digest for 30 min on 150 °C and for 1 h on 200°C plate. Dilute to 120 mL with water and stir for 1 min. Filter the leaching liquid through a GF/A (with suction). Wash the residue for 3 times each time with 10 mL 0.5 M HCl.
- 3) Transfer the solution to 250 mL centrifuge tube. Add 12.5% NH<sub>3</sub> to pH=7.5-8.0. Centrifuge and pour the supernatant to remove the Mg<sup>2+</sup> and Ca<sup>2+</sup>. Add 20 mL 6 M NaOH and stir for 5 min. Dilute to 200 mL, stir, centrifuge, and pour the supernatant to remove the amphoteric elements.
- 4) Add 5 mL 12 M HCl and transfer the solution to 500 mL beaker. Wash the tube with 1 M HCl. The volume is about 40 mL. Add 30 mL 30% H<sub>2</sub>O<sub>2</sub>. Heat the solution to remove the sulfur and reduce the volume to about 10 mL.
- 5) Transfer the solution back to the centrifuge tube and dilute the solution to 160 mL with water. Add 150 mg K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and stir for 20 min. Add 6 M NaOH to pH=10, centrifuge, and pour the supernatant.



- 6) The precipitate is dissolved in 10 mL 12 M HCl and 20 mL 6M HCl. The acidity is 6-8 M. Transfer the solution to a 250 mL separator. Extract with 50 mL 10% TIOA/xylene. Shake 5 min. Discard the organic phase (containing U, Po and Fe). Filter the aquatic phase to the centrifuge tube and dilute to 160 mL. Add 10 mg  $\text{Fe}^{+3}$  and  $\text{NH}_3$  to pH=10. Centrifuge and pour the supernatant.
- 7) The precipitate is dissolved in 3-5 mL 12 M HCl and dilute to 170 mL. Add 0.5 g  $\text{K}_2\text{S}_2\text{O}_5$  to sample and stir for 20 min. Add NaOH to pH=10, centrifuge, pour the supernatant.
- 8) The  $\text{Fe}(\text{OH})_2$  is dissolved in 1-3 mL 12 M HCl and measure the volume of solution. Acidify the to 8 M  $\text{HNO}_3$  with 14 M  $\text{HNO}_3$  ( $V_s / V_{\text{HNO}_3} = 1 / 1.3$ ). Add 50 mg  $\text{NaNO}_2$  and stir.
- 9) The solution is passed through an anion ion exchange column (13 x 1cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1,5mL/min.
- 10) Wash the column with 20 mL 8 M  $\text{HNO}_3$ . (Combine the passed solution and the 20 mL washes solution for americium analysis). \*Wash the column with 60 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl. The flow rate is about 1 mL/min.
- 11) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  + 0.1 g NaCl.
- 12) Add 4 mL 14 M  $\text{HNO}_3$  and evaporate to dryness.
- 13) The sample is dissolved in 6 mL 6 M HCl. Transfer the solution to 250 mL centrifuge tube. Wash the beaker and combine the solution to the tube. Dilute to 170 mL. Add 30 mg  $\text{Fe}^{3+}$ , 200 mg  $\text{K}_2\text{S}_2\text{O}_5$  and stir for 20 min. Add NaOH to pH=10, centrifuge and pour the supernatant.
- 14) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2 mL 12 M HCl and dilute to 10 mL with water. Add 13 mL 14.4 M  $\text{HNO}_3$  to 8 M  $\text{HNO}_3$ .
- 15) Repeat the steps 9).
- 16) Wash the column with 80 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl.
- 17) \*\* Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  + 0.6 g NaCl.
- 18) Preparation for electrodeposition.

## Plutonium procedure for fish, mussel and other biological samples

- 1) Dry and homogenize the samples.

- 2) Add 10 g fish powder,  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$ , 40 mL 14 M  $\text{HNO}_3$  and 30 mg  $\text{Fe}^{3+}$ . Cover the beaker with a glass disc and digest on 200°C plate for 3 h. Evaporate to dryness on 150 °C plate.
- 3) Burn at 550 °C in oven overnight. Add 40 mL aqua regia. Cover the beaker with glass disc and digest for 90 minutes. Dilute the solution to 100 mL with water and stir for 1 minute.
- 4) Filter the solution with GF/A to 250 mL plastic centrifuge tube. Wash the beaker and the paper with 30 mL 0.2 M HCl. Add  $\text{NH}_3$  the solution to pH=10. Centrifuge and pour off the supernatant.
- 5) The precipitate ( $\text{Fe}(\text{OH})_3$ ) is dissolved in 3-5 mL 12 M HCl. Dilute the solution to 170 mL. Add 0.3 g  $\text{K}_2\text{S}_2\text{O}_5$  and stir for 20 minutes. Add NaOH to pH = 10, centrifuge and pour the supernatant.
- 6)  $\text{Fe}(\text{OH})_2$  is dissolved in 2-3 mL 12 M HCl and measure the volume of sample. Acidify the solution to 8 M  $\text{HNO}_3$  with 14 M  $\text{HNO}_3$  ( $V_s : V_{\text{HNO}_3} = 1 : 1.3$ ).
- 7) The solution is passed through an anion ion exchange column (13 x 1 cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30 mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1,5 mL/min.
- 8) Wash the column with 20 mL 8 M  $\text{HNO}_3$ . (Combine the passed solution and 20 mL washing solution for americium analysis). Wash the column with 70 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl. The flow rate is 2-3 mL/min.
- 9) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH HCl}$  + 0.6 NaCl (without NaCl for ICPMS).
- 10) Prepare for electrodeposition.

## Plutonium procedure for seaweed

- 1) Dry the sample to constant weight by oven drying at 110 °C and homogenize the sample.
- 2) Add 10 g seaweed and 0.5 g NaCl to porcelain crucible and burn the sample at 700 °C in oven overnight.
- 3) Add  $^{242}\text{Pu}$ ,  $^{243}\text{Am}$ , 10 mL 12 M HCl and 4 mL 14 M  $\text{HNO}_3$ . Cover the porcelain crucible with a glass disc and digest for 30 min at 150°C. Add 30 mL 14 M  $\text{HNO}_3$  more and digest for 90 minutes at 200°C (or transfer the sample to a beaker for digesting). Add 30 mg  $\text{Fe}^{3+}$  and 50 mL  $\text{H}_2\text{O}$ . Stir for 30 seconds.

- 4) Filter the solution through a GF/A filter to centrifuge tube. Wash the beaker and the paper with 30 mL 0.2 M HCl. Add  $\text{NH}_3$  to the solution to pH = 8-9. Centrifuge and pour off the supernatant.
- 5) The precipitate is dissolved in 5 mL 12 M HCl and diluted to a 160 mL with  $\text{H}_2\text{O}$ . Add 150 mg  $\text{K}_2\text{S}_2\text{O}_5$ , stir and let stay for 20 min. Add NaOH to the solution to pH=10 and centrifuge. Pour off the supernatant.
- 6) Add 5 mL 12 M HCl to dissolve the sample. Transfer the solution to a separator funnel, wash the tube with 25 mL 6 M HCl and transfer to the funnel. Extract with 40 mL 10% TIOA/xylene. Shake with hand for 20 seconds and shake with machine for 5 min. Discard the organic phase.
- 7) Add 10 mg  $\text{Fe}^{3+}$  to the aquatic phase and dilute 150 mL. Add  $\text{NH}_3$  to pH=10, centrifuge, pour the supernatant.
- 8) The precipitate is dissolved in 5 mL 12 M HCl and dilute to 160 ml. Add 0.3 g  $\text{K}_2\text{S}_2\text{O}_5$  and stir for 20 minutes. Add NaOH to pH = 10, centrifuge and pour the supernatant.
- 9)  $\text{Fe}(\text{OH})_2$  is dissolved in 2-3 mL 12 M HCl and measure the volume of sample. Acidify the solution to 8 M  $\text{HNO}_3$  with 14 M  $\text{HNO}_3$  ( $V_s : V_{\text{HNO}_3} = 1 : 1.3$ ).
- 10) The solution is passed through an anion ion exchange column (13 x 1 cm, AG1-X<sub>4</sub> 100-200 mesh) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30 mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1,5 mL/min.
- 11) Wash the column with 20 mL 8 M  $\text{HNO}_3$ . (Combine the passed solution and 20 mL washing solution for americium analysis). Wash the column with 70 ml 8 M  $\text{HNO}_3$  and 50 ml 12 M HCl. The flow rate is 2-3 mL/min.
- 12) Strip with 80 ml 2 M HCl + 2 g  $\text{NH}_2\text{OH HCl}$  + 0.6 NaCl (without NaCl for ICPMS).
- 13) Prepare for electrodeposition.

## Plutonium procedure for 1-2 g sediment or soil

- 1) Transfer 1-2 g homogenized soil or sediment into a beaker. Burn at 550°C over night.
- 2) Add Am-243 and Pu-242 tracer, (0.2 g  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  for sand sample) and 20 mL aqua regia. Cover with glass disk. Digest for 30 min on 150 °C and for 1 h on 200°C plate. Dilute to 120 mL with water and stir for 1 min. Filter the leaching liquid through a GF/A (with suction) filter. Wash the residue for 3 times each time with 10 mL 0.5 M HCl.

- 3) Transfer the solution to 250 mL centrifuge tube. Add 12.5%  $\text{NH}_3$  to pH=7.5-8.0. Centrifuge and pour the supernatant to remove the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Add 20 mL 6 M NaOH and stir for 5 min. Dilute to 200 mL, centrifuge, pour the supernatant to remove the amphoteric elements.
- 4) The precipitate is dissolved in 5 mL 12 M HCl and dilutes the solution to 160 mL with water. Add 150 mg  $\text{K}_2\text{S}_2\text{O}_5$ . Stir for 20 min. Add NaOH to pH=10, centrifuge, and pour the supernatant.
- 5) The precipitate is dissolved in 5 mL 12 M HCl and 10 mL 6M HCl. The acidity is about 6 M. Transfer the solution to a 150 mL separator. Extract with 20 mL 10% TIOA/xylene. Shake 5 min. Discard the organic phase (containing U, Po and Fe).
- 6) Filter the aquatic phase to the centrifuge tube. Add 10 mg  $\text{Fe}^{+3}$  and dilute to 160 mL. Add 0.3 g  $\text{K}_2\text{S}_2\text{O}_5$  to sample and stir for 20 min. Add NaOH to pH=10, centrifuge, pour the supernatant.
- 7) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2-3 mL 12 M HCl and measure the volume of solution. Acidify the to 8 M  $\text{HNO}_3$  with 14 M  $\text{HNO}_3$  ( $V_s / V_{\text{HNO}_3} = 1 / 1.3$ ).
- 8) The solution is passed through a anion ion exchange column (13 x 1cm, AG1-X<sub>4</sub>, 100-200 mesh) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30 mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1.5 mL/min.
- 9) Wash the column with 20 mL 8 M  $\text{HNO}_3$ . (Combine the passed solution and the 20 mL washing solution for americium analysis. ). \*Wash the column with 50 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl. The flow rate is about 1 mL/min.
- 10) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  + 0.6 g NaCl.
- 11) Preparation for electrodeposition.

## Americium procedure for 10 g sediment, soil and 200 liters seawater

- 1) Add 10 mg  $\text{Fe}^{3+}$  to the americium fraction from the plutonium analysis and dilutes to 130 mL in a 250 mL centrifuge tube. Add  $\text{NH}_3$  to pH about 8, centrifuge and pour the supernatant.
- 2) The precipitate is dissolved in 3 mL 12 M HCl. Add 1 mL 30%  $\text{H}_2\text{O}_2$ , And 0.5 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and stir. Dilute to 140 mL with water. Add 30 mL 100 mg/mL  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  under stirring. Add 2.0 mL 25%  $\text{NH}_3$  to pH =1-1.5 to get white precipitate. Centrifuge for 10 min. at 3000 r.p.m. Pour off the supernatant. Wash the precipitate with 150 mL 0.1 M HCl + 3 mL 30%  $\text{H}_2\text{O}_2$ ,

3 mL 100 mg/mL  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and stir. Centrifuge for 10 minutes. Pour off the supernatant.

- 3) Add 1 mL 12 M HCl + 0.3 mL 14 M  $\text{HNO}_3$  + 10 mL 30%  $\text{H}_2\text{O}_2$ . Cover the tube with glass filter. Heat in water bath (on a  $220^\circ\text{C}$  plate) for 2 h to destroy the  $\text{C}_2\text{O}_4^{2-}$ . Add 2 mL 14 M  $\text{HNO}_3$  and heat for 10 min. Add 140 mL  $\text{H}_2\text{O}$ , 10 mg  $\text{Fe}^{+3}$  and stir. Add 3%  $\text{NH}_3$  to pH=6.5-7. Centrifuge for 10 minutes. Pour off the supernatant. Wash the precipitate with 160 mL  $\text{H}_2\text{O}$  pH=6.7 (NaOH) and stir for 20 minutes. Centrifuge and pour off the supernatant.
- 4) Add 3 mL 12 M HCl. Transfer the solution to 150 mL separator. Wash the beaker with 15 mL 6 M HCl and transfer the washing solution to the separator. Extract with 20 mL 10%TIOA/xylene (Po, U, Pu and  $\text{Fe}^{+3}$  in organic phase). Shake for 5 min. Discard the organic phase. Evaporate the aquatic phase to dryness. Add 5 ml 14 M  $\text{HNO}_3$  and evaporate to dryness. Add 3 ml 14 M  $\text{HNO}_3$  and evaporate to dryness again.
- 5) Add 10 mL 8 M  $\text{HNO}_3$  to dissolve the sample. The solution is passed through the column (12 x 1 cm, 100-200 mesh, AG1-X<sub>4</sub>) which is equilibrated with 20 mL 1 M  $\text{HNO}_3$  and 20 mL 8 M  $\text{HNO}_3$ . Wash the column with 15 mL 8 M  $\text{HNO}_3$ . Thorium is absorbed on the column. Collect the passed solution and washing solution. Evaporate the solution to dryness.
- 6) The sample is dissolved in 1.5 mL 14 M  $\text{HNO}_3$ . Add 0.3 mL 30%  $\text{H}_2\text{O}_2$ , stir and let stay for 2 min. Add 25 mL  $\text{CH}_3\text{OH}$  and stir. The solution is passed through the column (12 x 1 cm, AG1-X<sub>4</sub>, 100-200 mesh) which is equilibrated with 25 mL 1 M  $\text{HNO}_3$  and 20 mL 1 M  $\text{HNO}_3$ -93% methanol. The flow rate is about 1 mL/min.
- 7) Wash the column with 20 mL 1 M  $\text{HNO}_3$ -93% methanol, 100 mL 0.1 M HCl- 0.5 M  $\text{NH}_4\text{SCN}$ -80% methanol and 50 mL 1 M  $\text{HNO}_3$ -93% methanol.
- 8) Strip with 50 mL 1.5 M HCl - 86% methanol + 50 mg NaCl. Evaporate the stripped solution to dryness. Add 15 mL 14 M  $\text{HNO}_3$  and 2 ml 3 M  $\text{NaNO}_3$ . Cover the beaker with glass disc. Digest for 30 min. Evaporate to dryness.
- 9) Preparation for electrodeposition.

## Neptunium ( $^{237}\text{Np}$ ) procedure for 10 g sediment, soil and seawater

### Abstract

Procedures for determination of neptunium in soil, marine sediment and seawater samples are described. Iron hydroxide  $\text{Fe}(\text{OH})_2\text{-Fe}(\text{OH})_3$  is used for preliminary preconcentration of neptunium. Secondly, neptunium  $\text{Np}^{4+}$  and  $\text{Pu}^{3+}$  are separated by tri-isooctylamine (TIOA)/xylene extraction in 8-10 M HCl by redox with  $\text{SO}_3^{2-}\text{-Fe}^{3+}$ . Neptunium  $\text{Np}^{4+}$  and uranium  $\text{U}^{6+}$  are separated by back

extraction of  $\text{Np}^{4+}$  with 2 M HCl. Finally, the neptunium is purified from uranium and thorium by anion exchange in 8 M  $\text{HNO}_3$  and 12 M HCl. Neptunium  $\text{Np}^{3+}$  and uranium are further separated by stripping with 6 M HCl +  $\text{NH}_2\text{OHHCl}$ . Redox with  $\text{SO}_3^{2-}$ - $\text{Fe}^{3+}$  appeared to be an efficient way to obtain  $\text{Np}^{4+}$ . The decontamination factors of the procedure are  $4 \cdot 10^4$  for  $^{232}\text{Th}$ ,  $5.6 \cdot 10^4$  for uranium and  $1.6 \cdot 10^4$  for plutonium

## Principle

High valences of neptunium are reduced to  $\text{Np}^{4+}$  by  $\text{K}_2\text{S}_2\text{O}_5 + \text{FeCl}_3$  in 100 liters seawater at  $\text{pH}=2$ . The  $\text{Np}(\text{OH})_4$  and transuranium elements are carried by a  $\text{Fe}(\text{OH})_2$ - $\text{Fe}(\text{OH})_3$  precipitation at  $\text{pH}=10$ . The hydroxide precipitation is repeated twice, the first time to remove a large amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at  $\text{pH}=8$  in  $\text{NH}_3$  system and the second time to separate the amphoteric elements in a 0.3-0.5 M NaOH solution. In order to get rid of the large amount of sulfur from sulfite (especially in sediment), the sample solution is boiled with  $\text{H}_2\text{O}_2$  in 1 M HCl. The reaction is  $\text{S} + 2 \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$ . The  $\text{H}_2\text{SO}_3$  is decomposed to  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , which is evaporated, or the  $\text{H}_2\text{SO}_3$  is further oxidized to  $\text{H}_2\text{SO}_4$ .

Control of the valence of the neptunium plays an important role in the procedure. Neptunium is reduced to  $\text{Np}^{4+}$  by the redox system  $\text{SO}_3^{2-}$ - $\text{Fe}^{3+}$  and precipitated with  $\text{Fe}(\text{OH})_2$  which is dissolved in 10 M HCl.  $\text{NpCl}_6^{2-}$  and  $\text{UO}_2\text{Cl}_4^{2-}$  are extracted into 10% TIOA/xylene (The aquatic phase contains  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  are collected for Pu and Am analyses). Neptunium is backextracted in 2 M HCl solution and uranium is kept in the organic phase.  $\text{Np}^{4+}$  is prepared by adding  $\text{K}_2\text{S}_2\text{O}_5 + \text{FeCl}_3$  to the back extraction solution which is neutralized to  $\text{pH}=10$ . After centrifuging, the  $\text{Fe}(\text{OH})_2$  is dissolved in 1 mL 12 M HCl and acidified to 8 M  $\text{HNO}_3$ . The solution is passed through the anion exchange column. The column is eluted with 8 M  $\text{HNO}_3$  for separation of uranium and the column is eluted with 12 M HCl for thorium decontamination. Neptunium is stripped with 6 M HCl +  $\text{NH}_2\text{OH} \cdot \text{HCl}$  +  $\text{NH}_4\text{Cl}$ . After the stripping, 14.4 M  $\text{HNO}_3$  is added and the solution evaporated to dryness.

(a) The sample is dissolved in 4%  $\text{HNO}_3$  for ICPMS measurement

(b) The source for  $\alpha$ -measurement is prepared.

The chemical yield of  $^{237}\text{Np}$  is determined by internal standard addition, i.e. splitting the sample in two parts, adding known amount of  $^{237}\text{Np}$  to one of the aliquots, and then analysing the two parts under identical circumstances.

## Neptunium procedure for sediment and soil

- 1) Dry the sample to constant weight in an oven at  $110^\circ\text{C}$  and homogenise the sample.
- 2) Add 10 g sample to a 125 mL beaker and burn at  $550^\circ\text{C}$  in an oven overnight. Add  $^{239}\text{Np}$  tracer and 60 mL aqua regia to the sample. Stir for 1 min. Cover the beaker with a glass disc and digest for 30 min at  $150^\circ\text{C}$  and for

1 h at 200°C. Add 100 mL H<sub>2</sub>O, 0.2 g FeCl<sub>3</sub> and stir for 1 minute. Filter the sample through a GF/A filter by suction. Discard the residue.

- 3) Transfer the sample to 250 mL plastic centrifuge tube. Add NH<sub>3</sub> to pH=8-9, centrifuge, pour the supernatant (to remove the Ca<sup>2+</sup> and Mg<sup>2+</sup>). Add 20 mL 6 M NaOH, stir, dilute 180 mL, stir. Centrifuge and pour the supernatant.
- 4) The precipitate is dissolved in 5 mL 12 M HCl, dilute to 40 mL and transfer the solution a 500 mL beaker. Add 30 mL 30% H<sub>2</sub>O<sub>2</sub>. Digest for 15 minutes and evaporate to about 10 mL (to remove the sulphur).
- 5) Transfer the solution back the centrifuge tube and dilute to 170 mL. Add 0.5 g K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and stir for 20 minutes. Add NaOH to pH =10, centrifuge and pour the supernatant. The precipitate is dissolved in 12 M HCl (about 40 mL) and the last volume is up to 50 mL. The concentration of HCl should be 8-10 M.
- 6) Extract with 50 mL 10% TIOA/xylene. Shake for 5 min. Discard the aquatic phase (Pu<sup>3+</sup>, Am<sup>3+</sup> and Th). Wash the organic phase with 50 mL 10 M HCl. Shake for 5 min. Discard the aquatic phase.
- 7) Back-extract for 3 times, each time with 20 mL 2 M HCl + 2 drop 3 M NaCl. Shake 5 min Discard the organic phase (UO<sub>2</sub>Cl<sub>4</sub><sup>2-</sup> and PoCl<sub>6</sub><sup>2-</sup>). Filter the back extraction solution with GF/A into a centrifuge tube, and dilute the solution to 150 mL.
- 8) Add 30 mg Fe<sup>3+</sup> and 200 mg K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> to the solution. Stir for 20 min. Add NaOH to pH=10, centrifuge, and discard the supernatant.
- 9) The Fe(OH)<sub>2</sub>-Np(OH)<sub>4</sub> is dissolved in 2-3 mL 12 M HCl and measure the volume. Acidify to 8 M HNO<sub>3</sub> with 14 HNO<sub>3</sub> (V<sub>s</sub> : V<sub>HNO<sub>3</sub></sub> = 1 : 1.3 ). Stir and let stay for 20 min. The solution is passed through the anion exchange column (14 x 1 cm, 100-200 mesh, AG1-x<sub>4</sub>) which is equilibrated with 25 mL 1 M HNO<sub>3</sub> and 30 mL 8 M HNO<sub>3</sub>. The flow rate is 1 ml/min.
- 10) Wash the column with 80 mL 8 M HNO<sub>3</sub>(to remove U, Fe<sup>3+</sup>) and wash with 50 mL 12 M HCl (to remove Th<sup>4+</sup>)
- 11) Strip with 80 mL 6 M HCl + 2 g NH<sub>2</sub>OH·HCl.
- 12) Add 2 mL 14 M HNO<sub>3</sub> to the solution. Cover the beaker and digest for 30 min on 200°C plate. Evaporate the solution to dryness on a 150°C plate. Add 2 mL 14 M HNO<sub>3</sub> and evaporate to dryness and heat to volatise the NH<sub>4</sub>NO<sub>3</sub>.
- 13)
  - a) The sample is dissolved in 10 mL 4% HNO<sub>3</sub> for ICPMS measurement  
or
  - b) Add 2mL 3 M NaNO<sub>3</sub> and prepare for electrodeposition.

# Neptunium ( $^{237}\text{Np}$ ) procedure for 100 liters seawater

- 1) Add 100 mL 12 M HCl to 100 litres seawater to pH about 2. Add  $^{239}\text{Np}$  tracer, 2 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 100 g  $\text{K}_2\text{S}_2\text{O}_5$ . Stir with air bubbles for 30 min. Add NaOH to the seawater to pH=10. Let stay overnight.
- 2) Siphon the supernatant. Transfer the precipitate to a bottle (small tank) and acidify the sample to pH about 1 with HCl. Stir and let stay for 20 min to dissolve the  $\text{Ca}(\text{OH})_2$ . Add  $\text{NH}_3$  to pH=10 (to remove  $\text{Ca}^{2+}$ ). Filter the precipitate with GF/A under suction. Wash the precipitate with 100 mL NaOH pH=10.
- 3) The precipitate is dissolved in 40 mL 12 M HCl and 40 mL 14 M  $\text{HNO}_3$  in a 500 mL beaker. Cover the beaker with a glass disc and digest for 90 minutes on a 200°C plate. Dilute to 100 mL. Filter the solution with a GF/A to 250 ml plastic centrifuge tube. Add 25%  $\text{NH}_4\text{OH}$  to pH=10, centrifuge and pour the supernatant. Go to the step 4) of the sediment procedure.

## Procedure for simultaneous determination of $^{237}\text{Np}$ and $^{239,240}\text{Pu}$ in 10 g sediment or soil

### Application

Plutonium and neptunium are quantitatively scavenged by  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  in basic solution. In redox  $\text{SO}_3^{2-} - \text{Fe}^{3+}$  system in weak HCl solution, plutonium and neptunium are kept as  $\text{Pu}^{3+}$ ,  $\text{Np}^{4+}$  which are carried by  $\text{Fe}(\text{OH})_2$  at pH = 10. While the  $\text{Fe}(\text{OH})_2$  is dissolved in 2-3 mL 12 M HCl and then acidified to 8 M  $\text{HNO}_3$  with concentrated  $\text{HNO}_3$  (65%) the  $\text{Pu}^{3+}$  is oxidised to  $\text{Pu}^{4+}$  by  $\text{HNO}_3/\text{HNO}_2$  ( $E_0=0.94\text{V}$ ) and  $\text{HNO}_3/\text{N}_2\text{O}_4$  ( $E_0=0.79\text{V}$ ), and neptunium is still kept as  $\text{Np}^{4+}$ .  $\text{Np}(\text{NO}_3)_6^{2-}$  and  $\text{Pu}(\text{NO}_3)_6^{2-}$  are formed in the 8 M  $\text{HNO}_3$  solution. Both complexes are absorbed on the anion exchange column. Uranium is eluted with 8 M  $\text{HNO}_3$  and thorium with 12 M HCl. The Pu and Np are stripped with 2 M HCl + 2 g  $\text{NH}_2\text{OHHCl}$ , which reduces Pu and Np to +3 valence. The sample is evaporated to dryness and dissolved in 4%  $\text{HNO}_3$  for ICPMS measurement.

- 1) Transfer 10g of homogenized soil or sediment to a beaker. Burn at 550°C over night.
- 2) Add  $^{242}\text{Pu}$  tracer,  $^{243}\text{Am}$  (0.2 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  for sand sample) and 60 mL aqua regia. Cover with glass disk. Digest for 30 min at 150 °C and for 1 h on 200°C plate. Dilute to 120 mL with water and stir for 1 min. Filter the



leaching liquid through a GF/A (with suction). Wash the residue 3 times each time with 10 mL 0.5 M HCl and combine the washing solutions to filtrate.

- 3) Transfer the solution to 250 mL centrifuge tube. Add 12.5%  $\text{NH}_3$  to pH=10. Centrifuge and pour the supernatant to remove  $\text{Ca}^{2+}$ . Add 20 ml 6 M NaOH and stir for 5 min. Dilute to 200 mL, centrifuge, discard the supernatant to remove the amphoteric elements.
- 4) Add 5 mL 12 M HCl and transfer the solution to a 500 mL beaker. Wash the tube with 1 M HCl. The volume is about 40 ml. Add 30 mL 30%  $\text{H}_2\text{O}_2$  and heat to reduce the volume to about 10 mL (to remove the sulfur).
- 5) Transfer the solution back to the centrifuge tube and dilute the solution to 160 mL with water. Add 0.5 g  $\text{K}_2\text{S}_2\text{O}_5$ . Stir for 20 min. Add NaOH to pH=10, centrifuge, and discard the supernatant.
- 6) The  $\text{Fe}(\text{OH})_2$  is dissolved in about 3 mL 12 M HCl. Measure the volume of the solution. Acidify the solution to 8 M  $\text{HNO}_3$  with 14.4 M  $\text{HNO}_3$  ( $V_s / V_{\text{HNO}_3} = 1 / 1.3$ ).
- 7) The solution is passed through a anion ion exchange column (13 x 1cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 30 mL 1 M  $\text{HNO}_3$  and 30 mL 8 M  $\text{HNO}_3$ . The flow rate is about 1-1.5 mL/min.
- 8) Wash the column with 20 mL 8 M  $\text{HNO}_3$ . (Combine the passed solution and the 20 mL washing solution for americium analysis. ). \*Wash the column with 50 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl. The flow rate is about 1 mL/min.
- 9) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and 50 mL 0.5 M  $\text{HNO}_3$ .
- 10) Add 4 mL 65%  $\text{HNO}_3$  to decompose the  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and evaporate to dryness.
- 11) The sample is dissolved in 6 mL 6 M HCl. Transfer the solution to a 250 mL centrifuge tube. Wash the beaker and combine the solution to the tube. Dilute to 170 mL. Add 0.3 g  $\text{K}_2\text{S}_2\text{O}_5$ , 30 mg  $\text{Fe}^{3+}$  and stir for 20 min. Add NaOH to pH=10, centrifuge and discard the supernatant.
- 12) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2 mL 12 M HCl and dilute to 10 mL with water. Add 13 mL 14.4 M  $\text{HNO}_3$  to 8 M  $\text{HNO}_3$ .
- 13) Repeat step 7).
- 14) Wash the column with 70 mL 8 M  $\text{HNO}_3$  and 50 mL 12 M HCl.
- 15) Strip with 80 mL 2 M HCl + 2 g  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and 50 mL 0.5 M  $\text{HNO}_3$ .
- 16) \*Add 3 mL 2 M  $\text{NaNO}_3$ , 0.3 ml 18 M  $\text{H}_2\text{SO}_4$  and 4 mL 14.4 M  $\text{HNO}_3$  to the stripping solution. Evaporate to dryness at 150°C overnight. Heat at 400°C for 40 min. for electrodeposition.

\*Add 3 mL 14.4 M HNO<sub>3</sub> to percolate and evaporate to dryness. Add 5 mL 14.4 M HNO<sub>3</sub> and evaporate to dryness again. The sample is dissolved in 10 mL 4% HNO<sub>3</sub> for ICPMS measurement.

## Procedure for simultaneous determination of <sup>239,240</sup>Pu and <sup>237</sup>Np in 200 liters seawater

### On board the ship

- 1) Acidify 200 liters seawater to pH=2 with 200 mL 12 M HCl. Add 2 g FeCl<sub>3</sub>·6H<sub>2</sub>O, <sup>242</sup>Pu, <sup>243</sup>Am and 100 g K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>. Stir by bubbling for 1 h to reduce all plutonium valences to Pu<sup>3+</sup> and all neptunium valences to Np<sup>4+</sup>.
- 2) Basify the 200 liters seawater to pH about =10 with 800 mL 6 M NaOH (Dilute to 0.5-1 M) to precipitate Fe(OH)<sub>2</sub>-Pu(OH)<sub>3</sub>-Np(OH)<sub>4</sub>-Am(OH)<sub>3</sub>. Diluted NaOH is added to reduce the formation of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>. Let stay for 5 h or overnight. Siphon off the supernatant liquid to get about 5 liters of Fe(OH)<sub>2</sub> slurry.
- 3) Acidify the sample to about 0.1 M HCl with concentrated HCl (about 15 mL/liter) Transfer the sample to laboratory for analysis.

### In the laboratory

- 4) Slowly add 6% NH<sub>3</sub> to pH=10. Let stay overnight. Discard the supernatant liquid. Filter the precipitate on GF/A filter paper under suction (or centrifuge).
- 5) The precipitate is dissolved in 30 mL 12 M HCl + 30 mL 14.4 M HNO<sub>3</sub> in a 200 mL beaker. Cover the beaker with a glass disc and heat for 1-2 h to digest the sample.
- 6) Evaporate to about 30 ml and filter the solution with GF/A to a 250-mL centrifuge tube. Dilute to 120 mL. Add 25% NH<sub>4</sub>OH to pH about 10. Centrifuge, Pour the supernatant to remove the Ca<sup>2+</sup> and Mg<sup>2+</sup>.
- 7) The precipitate is dissolved in 5 mL 12 M HCl. Dilute the solution to 160 mL with water. Add 0.5 g K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>. Stir with magnetic stirrer for 20 min. Add NaOH to pH=10, centrifuge, and discharged the supernatant.
- 8) The Fe (OH)<sub>2</sub> is dissolved in 5 mL 12 M HCl. Measure the volume of the solution. Acidify to 8 M HNO<sub>3</sub> with 14 M HNO<sub>3</sub> (V<sub>s</sub> / V<sub>HNO<sub>3</sub></sub> = 1 / 1.3).
- 9) The solution is passed through an anion ion exchange column (13 x 1cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 30 mL 1 M HNO<sub>3</sub> and 30mL 8 M HNO<sub>3</sub>. The flow rate is about 1-1,5mL/min.

- 10) Wash the column with 20 mL 8 M HNO<sub>3</sub>. (Combine the passed solution and the 20 mL washes solution for americium analysis. ). \*Wash the column with 50 mL 8 M HNO<sub>3</sub> and 50 mL 12 M HCl. The flow rate is about 1 mL/min.
- 11) Strip with 80 mL 2 M HCl + 2 g NH<sub>2</sub>OH.HCl + 50 mL 0.5 M HNO<sub>3</sub>.
- 12) Add 4 mL 14.4 M HNO<sub>3</sub> to decompose and evaporate to dryness.
- 13) The sample is dissolved in 6 mL 6 M HCl. Transfer the solution to a 250 mL centrifuge tube. Wash the beaker with 30 mL 0.5 M HCl and combine the solution to the tube. Dilute to 170 mL. Add 0.3 g K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, 30 mg Fe<sup>3+</sup> and stir for 20 min. Add NaOH to pH=10, centrifuge and discharge the supernatant.
- 14) The Fe(OH)<sub>2</sub> is dissolved in 2 mL 12 M HCl and dilute to 10 mL with water. Add 13 mL 14.4 M HNO<sub>3</sub> to 8 M HNO<sub>3</sub>.
- 15) Repeat step 9).
- 16) Wash the column with 70 mL 8 M HNO<sub>3</sub> and 50 mL 12 M HCl.
- 17) Strip with 80 mL 2 M HCl + 2 g NH<sub>2</sub>OH.HCl + 50 mL 0.5 M HNO<sub>3</sub>.
- 18) a) Add 4 mL 14.4 M HNO<sub>3</sub> and evaporate dryness. Add 5 mL 14.4 M HNO<sub>3</sub> and evaporate to dryness. The sample is dissolved in 10 mL 4% HNO<sub>3</sub> for ICPMS measurement.
- 19) Add 3 mL 2 M NaNO<sub>3</sub>, 0.3 mL 18 M H<sub>2</sub>SO<sub>4</sub> and 4 mL 14.4 M HNO<sub>3</sub> to the stripping solution. Evaporate to dryness on a 150°C plate overnight. Heat at 400°C for 40 min for electrodeposition.

## Determination of uranium in soil and sediment

### Application

The leaching solution of an environmental sample (or after polonium is removed by thermal deposition) is treated with FeCl<sub>3</sub> + Na<sub>2</sub>SO<sub>3</sub> and acidified to 6-10 M HCl. The solution is passed through the anion exchange column. UO<sub>2</sub>Cl<sub>4</sub><sup>2-</sup>, FeCl<sub>4</sub><sup>-</sup> and PoCl<sub>6</sub><sup>2-</sup> are absorbed on the column and Th<sup>4+</sup>, Pu<sup>3+</sup>, Am<sup>3+</sup>, Fe<sup>2+</sup> and bulk material are passed through.

The column is eluted with 6 M HCl for clean Th<sup>4+</sup>, Pu<sup>3+</sup>, Am<sup>3+</sup> and Fe<sup>2+</sup>, and with 5 M HNO<sub>3</sub>-9% H<sub>2</sub>O<sub>2</sub> to get off the Fe<sup>3+</sup>.

Uranium is stripped with 5 M HNO<sub>3</sub> and polonium is removed by thermal deposition before prepared for uranium electrodeposition.

- 1) 0.3-1 g soil or sediment,  $^{232}\text{U}$ ,  $^{208}\text{Po}$  and 12 aqua regia are added to 150 mL beaker. The sample is stirred to homogeneity and the beaker is covered with a glass disc, and heated for 90 minutes on 150-200°C plate. The isotope exchange should be completed.
- 2) Dilute the leaching solution to 100 ml with water and stir. Filter the solution through a filter GF/A into centrifuge tube.
- 3) Add 25%  $\text{NH}_3$  to pH=10 to form  $\text{Fe}(\text{OH})_3$  and centrifuge for 10 min. at 300 r.p.m. Discard the supernatant.
- 4) The  $\text{Fe}(\text{OH})_3$  is dissolved in 1 mL 12 M HCl and the solution is transferred to glass tube, and the centrifuge tube is washed with 30 ml 0.1 M HCl and combined to the glass tube for polonium thermal deposition on silver disc (see polonium analysis) which is ready for polonium  $\alpha$ -measurement.
- 5) The solution is transferred to beaker. Add 3 ml 14 M  $\text{HNO}_3$  to the sample and evaporate to dryness. The sample is dissolved in 6 ml 6 M HCl and transferred to the centrifuge tube, and diluted to 150 ml. Add 0.3 g  $\text{Na}_2\text{SO}_3$  stir with magnetic stirrer for 10 min and adjusted with NaOH to pH=10 to form  $\text{Fe}(\text{OH})_2$  and centrifuge for 10 min. Discard the supernatant.
- 6) The  $\text{Fe}(\text{OH})_2$  is dissolved in 2 mL HCl. Measure the volume of the solution. Acidify the solution to 6-8 M HCl.
- 7) The solution is passed through the column (14 x 1 cm, 100-200 mesh AG1-X<sub>4</sub>) which is equilibrated with 20 mL 6 M HCl. ( $\text{UO}_2\text{Cl}_4^{2-}$ ,  $\text{FeCl}_4^-$  and  $\text{PoCl}_6^{2-}$  are absorbed on the column and  $\text{Th}^{4+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$  and bulk material are passed through)
- 8) The column is eluted with 50 mL 6 M HCl to clean for  $\text{Th}^{4+}$ ,  $\text{Fe}^{2+}$  and  $\text{Pu}^{3+}$ . and with 25 mL 5 M  $\text{HNO}_3$ -9%  $\text{H}_2\text{O}_2$  (3 mL by 3 mL) to clean for  $\text{Fe}^{3+}$ . Pressurised air is applied to the liquid surface of the column to get rid off the large amount of bubbles.
- 9) Strip with 50 mL 5 M  $\text{HNO}_3$ .
  - a) Evaporate the eluate to dryness. Add 5 mL  $\text{HNO}_3$  and evaporate to dryness again. The sample is dissolved in 10 mL 4%  $\text{HNO}_3$  for ICPMS measurement.
  - b) ml 3 M  $\text{NaNO}_3$  and 0.3 mL 18 M  $\text{H}_2\text{SO}_4$  are added to the strip solution and evaporated to dryness on 150 °C. Heat at 400 °C for 40 min. for electrodeposition

# Determination of uranium in food products

- 1) Add 10 g ash of potato (or brown bread, cod, beef and 5 g ash of milk) to a 200 mL beaker and cover with a glass disc to protect contamination of U and Th from oven wall. Burn at 600 °C in oven for 3 days.
- 2) Add tracer  $^{232}\text{U}$ ,  $^{229}\text{Th}$ ,  $^{208}\text{Po}$  1g  $\text{NaNO}_3$ , 10 mL 12 M HCl and 10 mL 14 M  $\text{HNO}_3$  to the beaker which is covered with a glass disc. Heat at 150 °C for 1 h and evaporate to dryness. Add 10 mL 14 M  $\text{HNO}_3$  and evaporate dryness again. Heat at 200 °C for 10 min and 300 °C for 1 h.
- 3) Cover the beaker with the glass disc and burn at 550 °C over night. Add 40 mL aqua regia and digest for 30 min on 150 °C and for 1 h on 200 °C.
- 4) Dilute to 120 mL and add 10 mg  $\text{Fe}^{3+}$ . Filter the sample through a GF/A filter to 250 mL plastic centrifuge tube. Add 25%  $\text{NH}_3$  to pH =10 and centrifuge, pour off the supernatant.
- 5) The precipitate is dissolved in 10 mL HCl and diluted to 150 mL, and 0.3 g  $\text{NaSO}_3$  is added during stirring for 10 min. Add NaOH to pH = 10, centrifuge and discard the supernatant.
- 6) The precipitate is dissolved in 10 mL 12 HCl and the volume of sample solution is measured. Then acidify to 6 M HCl.
- 7) The solution is passed through the column (14x1 cm, Ag1-X<sub>4</sub>, 100-200 mesh) which is equilibrated with 30 mL 6 M HCl and eluted with 60 mL 6 M HCl, and 25 mL 5 M  $\text{HNO}_3$ -9%  $\text{H}_2\text{O}_2$  (with pressure air to get rid of the bobbles from the column.)
- 8) \*First strip with 50 mL 5 M  $\text{HNO}_3$  for uranium.
- 9) Evaporate the uranium fraction to dryness and add 5 mL 12 M HCl. Evaporate to dryness again. The sample is dissolved in 30 mL 0.3 M HCl for polonium thermal deposition in order to avoid Po contamination in the U-fraction. Discard the silver disc with the polonium.
- 10) Transfer the solution to the beaker and add 4 mL 14 M  $\text{HNO}_3$ , and evaporate to dryness. The sample is dissolved in 15 mL 6 M HCl.
- 11) The solution is passed through the column (14x1 cm, Ag1-X<sub>4</sub>, 100-200 mesh)
- 12) which is equilibrated with 30 mL 6 M HCl. The column is eluted with 60 mL M HCl, and 25 mL 5 M  $\text{HNO}_3$ -9%  $\text{H}_2\text{O}_2$  (with pressure to get off the bobbles from the column.)

13) Strip with 50 mL 5 M HNO<sub>3</sub>.

a) The sample is evaporated to dryness and dissolved in 10 mL 4% HNO<sub>3</sub> for ICPMS measurement.

b) Add 0.3 mL 18 M H<sub>2</sub>O<sub>4</sub> and 2 mL 3 M NaNO<sub>3</sub> and evaporate to dryness. Heat at 400 °C for 40 min. for electrodeposition.

\* (The second strip with 5 mL H<sub>2</sub>O, 6 mL 1 M NaOH and 100 mL 0.5 M HNO<sub>3</sub>. Evaporate to dryness. Add 5 mL 12 M HCl and evaporate to dryness again. The sample is dissolved in 3 mL 0.3 M HCl with 1 g NH<sub>2</sub>OHHCl for polonium thermal deposition).

## Determination of thorium in soil and sediment

### Application

The sample solution is free from Cl<sup>-</sup> by repeat evaporating and boiled in 2 M HNO<sub>3</sub> with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to oxidise to PuO<sub>2</sub><sup>2+</sup>. In 8 M HNO<sub>3</sub>, Th(NO<sub>3</sub>)<sub>6</sub><sup>-2</sup> is absorbed on an anion exchange column, while PuO<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub><sup>2-</sup> and UO<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub><sup>2-</sup> is passed through. Thorium is stripped with 8 M HCl.

### Procedure

- 1) 0.3-1 g soil or sediment, <sup>229</sup>Th tracer and 12 mL aqua regia are added to 150 mL beaker. The sample is stirred to homogeneity and the beaker is covered with a glass disc, and heated for 90 minutes on a 150-200°C plate. The isotope exchange should be completed.
- 2) Dilute the leaching liquid to 100 mL with water and stir. Filter the solution through a GF/A filter to 250 mL plastic centrifuge tube.
- 3) Add 25% NH<sub>3</sub> to pH=10 to form Fe(OH)<sub>3</sub> and centrifuge for 10 min. at 300 r.p.m. Pour off the supernatant.
- 4) The sample is dissolved in 5 mL 14 M HNO<sub>3</sub> and transferred to beaker. Wash the tube with 5 mL 14 M HNO<sub>3</sub> and combine the solution to the beaker. Evaporate the solution to near dryness. Add 5 mL 14 M HNO<sub>3</sub> and evaporate to near dryness again.
- 5) Add 5 mL 2 M HNO<sub>3</sub> and 0.3 g Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, stir and evaporate to near dryness to get PuO<sub>2</sub><sup>2+</sup>. The sample is dissolved in 15 mL 8 M HNO<sub>3</sub>.
- 6) The solution is passed through the anion exchange column (14 x 1 cm, AG1-X4.100-200 mesh) which is equilibrated with 30 mL 2 M HNO<sub>3</sub> and 30 mL 8 M HNO<sub>3</sub>. Th(NO<sub>3</sub>)<sub>6</sub><sup>-2</sup> is absorbed on the column while

$\text{PuO}_2(\text{NO}_3)_4^{2-}$  and  $\text{UO}_2(\text{NO}_3)_4^{2-}$  is passed through the column. Elute the column with 70 mL 8 M  $\text{HNO}_3$ .

- 7) Strip with 60 mL 8 M  $\text{HCl}$  ( $\text{PuO}_2\text{Cl}_4^{2-}$  and  $\text{UO}_2\text{Cl}_4^{2-}$  are absorbed on the column).
  - a) Evaporate to dryness. Add 10 mL 65%  $\text{HNO}_3$  and evaporate to dryness again. The sample is dissolved in 10 mL in 4%  $\text{HNO}_3$  for ICPMS measurement.
  - b) Add 0.3 mL  $\text{H}_2\text{SO}_4$  and 2 mL 3 M  $\text{NaNO}_3$  to the strip solution and evaporate to dryness. Heat at 400 °C for 40 minutes. It goes to electrodeposition and  $\alpha$ - measurement.

## Determination of thorium in food products

- 1) Add 10 g ash of potato (or brown bread, cod, beef and 5 g ash of milk) to a 200 beaker and cover with a glass disc to protect from U and Th contamination from oven wall. Burn at 600 °C in oven for 3 days.
- 2) Add  $^{229}\text{Th}$  tracer, 1g  $\text{NaNO}_3$ , 10 mL 12 M  $\text{HCl}$  and 10 mL 14 M  $\text{HNO}_3$  to the beaker, which is covered with a glass disc. Heat at 150 °C for 1 h and evaporate to dryness. Add 10 mL 14 M  $\text{HNO}_3$  and evaporate to dryness again. Heat at 200 °C for 10 min and 300 °C for 1 h.
- 3) Cover the beaker with a glass disc and burn at 550 °C over night. Add 40 mL aqua regia and digest for 30 min at 150 °C and for 1 h at 200 °C.
- 4) Dilute to 50 mL. Add 10 mg  $\text{Fe}^{3+}$  and filter the sample through a GF/A filter to a 250 mL plastic centrifuge tube. Add 25%  $\text{NH}_3$  to pH =10 and centrifuge. Discard the supernatant.
- 5) The precipitate is dissolved in 10 mL 14  $\text{HNO}_3$ . 0.3 g  $\text{Na}_2\text{S}_2\text{O}_8$  is added and evaporated to near dryness. Add 10 mL 65%  $\text{HNO}_3$  and evaporate to near dryness. Repeat by adding 10 mL 65%  $\text{HNO}_3$  two times to get a  $\text{Cl}^-$  free from sample.
- 6) The sample is dissolved in 30-40 mL 8 M  $\text{HNO}_3$  and passed through the column (14 x 1 cm, AG1-X<sub>4</sub>, 100-200 mesh) which is equilibrated with 30 mL 2 M  $\text{HNO}_3$  and 30 mL 8 M  $\text{HNO}_3$ . Elute the column with 70 mL 8 M  $\text{HNO}_3$ .
- 7) Strip with 60 mL 8 M  $\text{HCl}$ .
  - a) Evaporate the stripped solution to dryness. Add 10 mL 65%  $\text{HNO}_3$  and evaporate to dryness again. The sample is dissolved in 10 mL 4%  $\text{HNO}_3$  for ICPMS measurement.

b) Add 0.3 mL  $\text{H}_2\text{SO}_4$  and 2 mL 3 M  $\text{NaNO}_3$  to the percolate and evaporate to dryness. Heat at 400 °C for 40 minutes. It goes to electrodeposition step and  $\alpha$ -measurement.

## Determination of $^{99}\text{Tc}$ in 50 liters seawater

### Abstract

A procedure for the determination of  $^{99}\text{Tc}$  in seawater is described. Technetium is extracted by anion exchange directly from the seawater. Purification for ruthenium is accomplished by elution with 1 M  $\text{NaOH}$ -0.1 M  $\text{EDTA}$ - $\text{NaClO}$ . Finally, technetium is further purified by  $\text{Fe}(\text{OH})_3$  and  $\text{TIOA}$ /xylene extraction. The chemical yield is 70-80%.

### Principle

After filtering the seawater is passed through a AG1- $\text{X}_4$  anion exchange column. The  $\text{TcO}_4^-$  is very strongly absorbed on an anion exchange AG1- $\text{X}_4$  and  $\text{RuCl}_4^-$  is also absorbed on the anion exchange column. Ruthenium is eluted by 1 M  $\text{NaOH}$ -0.1 M  $\text{EDTA}$ - $\text{NaClO}$  from the anion column. During the elution,  $\text{Ru}^{3+}$  is oxidized to  $\text{Ru}^{4+}$  by  $\text{NaClO}$  and the  $\text{RuCl}_4^-$  is destroyed. The  $\text{Ru}^{4+}$  forms a chelate complex  $\text{Ru-EDTA}$ , which as a neutral compound is eluted from the column. The  $\text{TcO}_4^-$  is still strongly absorbed on the anion column. The  $\text{TcO}_4^-$  is stripped by (65%)  $\text{HNO}_3$  from the column. U, Th, Pu, Am and Po are very efficiently scavenged by  $\text{Fe}(\text{OH})_3$  from the  $\text{TcO}_4^-$  solution. The technetium is further purified by  $\text{TIOA}$ /xylene extraction in 1 M  $\text{H}_2\text{SO}_4$ . The sample is finally electro-deposited on stainless steel disc and  $\beta$ -counted. The yield is determined by a  $^{99\text{m}}\text{Tc}$  tracer.

The chemical yield of procedure is 70-80%. A decontamination factor for ruthenium of  $> 2 \cdot 10^5$  was obtained by repeating the anion exchange twice.

### Technetium-99 procedure for 50 liters seawater

- 1) Filter 50 liters seawater through filters and add  $^{99\text{m}}\text{Tc}$ . Stir to allow the isotope exchange to be completed. Let stay for 30 min.
- 2) The 50 liters seawater is passed through a column (16 · 2.5 cm AG1- $\text{X}_4$ , 100-200 mesh). The flow rate is 40-42 mL/min. It takes 22-23 hours.
- 3) Wash the column with 100 mL  $\text{H}_2\text{O}$ , 50 mL 1 M  $\text{NaOH}$  -0.1 M  $\text{EDTA}$ - 10 mL 15%  $\text{NaClO}$ , 150 mL 1 M  $\text{NaOH}$ -0.1 M  $\text{EDTA}$ -15 mL 15% $\text{NaClO}$ (for Ru decontamination), 100 mL 1 M  $\text{NaOH}$ , 100 mL  $\text{H}_2\text{O}$  and 500 mL 1 M  $\text{HNO}_3$ .



- 4) Strip with 200 mL 14.4 M (65%)  $\text{HNO}_3$  + 0.1 g  $\text{NaNO}_3$ . The flow rate is about 4 mL/min (the total stripping time is about 50 min).
- 5) Reduce the 200 mL stripping solution to 1 mL by heating. Add 0.5 mL 5 M  $\text{H}_2\text{SO}_4$  and dilute to 20 mL with  $\text{H}_2\text{O}$ . Add 2 mL 15%  $\text{NaClO}$ . Heat for 10 min.
- 6) Dilute to 30 mL. Add 0.2 mL (10 mg/mL)  $\text{AgNO}_3$  and 0.5 mL (10 mg/mL)  $\text{FeCl}_3$ . Add  $\text{NaOH}$  to pH=9. Heat for 5 minutes and add 0.5 mL  $\text{NaClO}$  (if the sample solution becomes black, add more  $\text{NaClO}$ ).
- 7) Filter the solution. Wash the precipitate 3 times, each time with 3 mL water pH=9( $\text{NaOH}$ ). Discard the precipitate (U, Th, Pu, Am, Po and Np).
- 8) Add 5 mL 10 M  $\text{H}_2\text{SO}_4$  and 1 g  $\text{K}_2\text{S}_2\text{O}_8$ . Dilute the solution to 50 mL with water. Transfer the solution to a 250 mL separator.
- 9) Extract with 40 mL 10% TIOA (tri-isooctylamine)/xylene. Shake for 5 min. Wash the organic phase 2 times, each time with 40 mL  $\text{H}_2\text{O}$ . Shake for 5 min (for U, Th decontamination).
- 10) Back extract with 20 mL 2 M  $\text{NaOH}$ . Shake for 2 min. Second back extract with 5 mL 0.5 M  $\text{NaOH}$  and shake for 2 min.
- 11) Evaporate the solution to 20 mL for electrodeposition. The current is 150  $\text{mA}/\text{cm}^2$ . It takes at least 5 h or overnight.
- 12) Clean the disc for  $\text{NaOH}$  by dipping it into the  $\text{H}_2\text{O}$  for times (hold it with tweezers), each time for 2 seconds. Heavy flushing will cause loss activity. The chemical yield is 70-80%.  $\beta$ -Counting is carried out after 7 days.

## Technetium-99 procedure for 200 liters seawater

- 1) Filter 200 liters seawater through filters and add  $^{99\text{m}}\text{Tc}$ . Stir to allow the isotope exchange to be completed. Let stay for 30 min.
- 2) The 200 liters seawater is passed through a column (16 X 4 cm AG1-X<sub>4</sub>, 100-200 mesh). The flow rate is 145-150 mL/min. It takes 22-23 hours.
- 1) Wash the column with 400 mL  $\text{H}_2\text{O}$ , 200 mL 1 M  $\text{NaOH}$  -0.1 M EDTA+ 40 mL 15%  $\text{NaClO}$ , 600 mL 1 M  $\text{NaOH}$ -0.1 M EDTA-60 mL 15% $\text{NaClO}$  (for Ru decontamination), 400 mL 1 M  $\text{NaOH}$ , 400 mL  $\text{H}_2\text{O}$  and 1000 mL 1 M  $\text{HNO}_3$ .
- 2) Strip with 600 mL 14.4 M (65%)  $\text{HNO}_3$  + 0.1 g  $\text{NaNO}_3$ . The flow rate is about 12 mL/min (the total stripping time is about 50 min). (On boat: meas-

ure the chemical yield of  $^{99m}\text{Tc}$ . Transfer the sample to laboratory and add  $^{99m}\text{Tc}$  again for analysis).

- 3) Reduce the 600 mL stripping solution to 1 mL by heating. Add 0.5 mL 5 M  $\text{H}_2\text{SO}_4$  and dilute to 20 mL with  $\text{H}_2\text{O}$ . Add 2 mL 15%  $\text{NaClO}$ . Heat for 10 min.
- 4) Dilute to 30 mL. Add 0.2 mL (10 mg/mL)  $\text{AgNO}_3$  and 0.5 mL (10 mg/mL)  $\text{FeCl}_3$ . Add  $\text{NaOH}$  to  $\text{pH}=9$ . Heat for 5 minutes and add 0.5 mL  $\text{NaClO}$ . If the sample solution becomes black ( $\text{TcO}_4^- \rightarrow \text{Tc}^{4+}$ ), add more  $\text{NaClO}$  ( $\text{Tc}^{4+} \rightarrow \text{TcO}_4^-$ ).
- 5) Filter the solution. Wash the precipitate 3 times, each time with 3 mL water  $\text{pH}=9(\text{NaOH})$ . Discard the precipitate (U, Th, Pu, Am, Po and Np).
- 6) Add 5 mL 10 M  $\text{H}_2\text{SO}_4$  and 1 g  $\text{K}_2\text{S}_2\text{O}_8$ . Dilute the solution to 50 mL with water. Transfer the solution to a 250 mL separator.
- 7) Extract with 40 mL 10% TIOA (tri-isooctylamine)/xylene. Shake for 5 min. Wash the organic phase 2 times, each time with 40 mL  $\text{H}_2\text{O}$ . Shake for 5 min (for U, Th decontamination).
- 8) Back extract with 20 mL 2 M  $\text{NaOH}$ . Shake for 2 min. Second back extract with 5 mL 0.5 M  $\text{NaOH}$  and shake for 2 min.
- 9) Evaporate the solution to 20 mL for electrodeposition. The current is 150  $\text{mA}/\text{cm}^2$ . It takes at least 5 h or overnight.
- 10) Clean the disc for  $\text{NaOH}$  by dipping it into the  $\text{H}_2\text{O}$  for times (hold it with tweezers), each time for 2 seconds. Heavy flushing will cause loss activity. The chemical yield is 70-80%.  $\beta$ -Counting is carried out after 7 days.

## Technetium ( $^{99}\text{Tc}$ ) procedure for seaweed-A new method

### Principle

In order to avoid the volatilization of technetium at high temperatures, a wet ash method was developed for seaweed analysis.

Seaweed is carbonized by concentrated  $\text{H}_2\text{SO}_4$ . Afterwards the sample is digested by concentrated  $\text{HNO}_3$ . After that the normal procedure is followed.

### Procedure for 10 g seaweed

- 1) Add 10 g fine dry seaweed power (ground with blender for 1 min) and 20 mL 18 M  $\text{H}_2\text{SO}_4$  in a flask. Stir until completely mixed. Let stay at least for 1 h or several days.

- 2) The seaweed is carbonised by concentrated  $\text{H}_2\text{SO}_4$ . Add  $^{99\text{m}}\text{Tc}$ , 0.5 mL 10 mg/mL  $\text{FeCl}_3$  0.3 mL 10 mg/mL  $\text{AgNO}_3$  and 1 g  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . Stir to homogeneity.
- 3) Add conc.  $\text{HNO}_3$  (65%) drop by drop to the flask. Be careful, the reaction is very strong. Continuously add conc.  $\text{HNO}_3$  (65%) (per g /6-8 mL  $\text{HNO}_3$ ) until the reaction is calm.
- 4) Heat the solution for 2 h (if the solution becomes black colour, add more  $\text{HNO}_3$ ). The solution becomes greenish. Transfer the solution to a 500 mL beaker and dilute to 200 mL. Add 10 g  $\text{K}_2\text{S}_2\text{O}_8$  and heat to boiling for 15 minutes, then dilute to 300 mL.
- 5) Add 6 M  $\text{NaOH}$  to the solution until  $\text{pH}=12$ . Filter the solution with GF/F 15 cm with suction and dilute to about 1000 mL. The solution is passed through the column (12 x 1.5 cm AG 1- $\text{X}_4$  100-200 mesh) The flow rate is 1-2 mL/min.
- 6) Wash the column with 20 mL  $\text{H}_2\text{O}$ , 40 mL 1 M  $\text{NaOH}$  – 0.1 M  $\text{EDTA}$  + 8 mL 15%  $\text{NaClO}$ , 30 mL 1 M  $\text{NaOH}$ , 20 mL  $\text{H}_2\text{O}$  and 100 mL 1 M  $\text{HNO}_3$ .
- 7) Strip the  $^{99}\text{Tc}$  with 60 mL 65%  $\text{HNO}_3$  + 0.1 g  $\text{NaNO}_3$ . The flow rate is about 1 mL/min
- 8) Evaporate the solution to 1 mL. Add 4 mL 10 M  $\text{H}_2\text{SO}_4$  and dilute to 30 mL, and add 1 g  $\text{K}_2\text{S}_2\text{O}_8$ . Transfer the solution to a 150 mL separator. Wash the beaker with 10 mL  $\text{H}_2\text{O}$  and transfer to the separator.
- 9) Add 40 mL 10%  $\text{TIOA}$ /xylene and shake 3 min. Wash the organic phase 2 times each time with 40 mL  $\text{H}_2\text{O}$  and shake for 5 min.(for U, Th decontamination)
- 10) Back extract with 20 mL 2 M  $\text{NaOH}$  and shake for 2 min. Second time back extract with 5 mL 0.5 M  $\text{NaOH}$  and shake for 2 min.
- 11) Evaporate the solution to 20 mL for electrodeposition. The current is 300  $\text{mA}/2\text{cm}^2$  the time is at least 5 h or overnight.
- 12) Clean the disc for  $\text{NaOH}$  by dipping it (hold with tweezers) careful for 2seconds in 100 mL  $\text{H}_2\text{O}$ . Heavy flushing will cause loss of activity. The chemical yield is 80-95.

# Determination of $^{210}\text{Po}$ and $^{210}\text{Pb}$ in mussel, fish, sediment and petroleum

## Abstract

A procedure for the determination of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in mussel, fish, sediment and petroleum has been developed. The sample is digested with  $\text{HNO}_3$  and  $\text{HCl}$ , and further digested with  $\text{H}_2\text{O}_2$  in 1 M  $\text{HCl}$ . After wetashing the  $^{210}\text{Po}$  is deposited on a silver disc by thermal decomposition.

Lead-210 is determined by ingrowth of  $^{210}\text{Po}$  from  $^{210}\text{Pb}$ . A rapid method for separation of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  has been developed utilising extraction with Triisooctylamine (TIOA)/xylene in  $\text{HCl} + \text{H}_2\text{O}_2$ .  $\text{PoCl}_6^{2-}$ ,  $\text{UO}_2\text{Cl}_4^{2-}$  and  $\text{FeCl}_4^-$  are extracted into TIOA and  $^{210}\text{Pb}$  remains in aquatic solution for  $^{210}\text{Po}$  ingrowth.

## Principle

The sample is digested with  $\text{HNO}_3 + \text{HCl}$  and evaporated to dryness. The organic matter is further digested with  $\text{H}_2\text{O}_2$  in 1 M  $\text{HCl}$ . Polonium is deposited on a silver disc in a  $\text{H}_2\text{OH}\cdot\text{HCl} - 0.3\text{-}0.5$  M  $\text{HCl}$  solution and analysed by  $\alpha$ -spectrometry.

Lead-210 is determined by ingrowth of  $^{210}\text{Po}$  from  $^{210}\text{Pb}$ . After the deposition, the sample is treated with  $\text{H}_2\text{O}_2$  and evaporated to about 5 mL, and acidified to 10 M  $\text{HCl}$ .  $\text{PoCl}_6^{2-}$ ,  $\text{UO}_2\text{Cl}_4^{2-}$  and  $\text{FeCl}_4^-$  are extracted into 5%TIOA/xylene and  $^{210}\text{Pb}$  remains in the aquatic solution, which is kept for half a year for the ingrowth of  $^{210}\text{Po}$  from  $^{210}\text{Pb}$ . Finally the  $^{210}\text{Po}$  from ingrowth is deposited on a silver disc and  $\alpha$ -counted. Lead-210 is obtained from a calculation of the  $^{210}\text{Po}$  ingrowth.(see Appendix -2)

## Procedure for polonium-210

1. To 10 g flesh of mussel (fish) in a 500 mL flask,  $^{208}\text{Po}$ , 25 mL 14 M  $\text{HNO}_3$ , 5 mL 12 M  $\text{HCl}$  and 0.3 g  $\text{NaCl}$  are added.

Condense for 5 h on 250°C plate to digest the flesh. Evaporate to dryness at 120-150 °C plate. Add 10 mL 30%  $\text{H}_2\text{O}_2$  1 mL 12 M  $\text{HCl}$  and evaporate to dryness on a 130°C plate. Add 10 mL 12 M  $\text{HCl}$  and evaporate to dryness on 120-150°C plate. Go to step 2.

(Sediment: Use 0.2- 0.5 g sediment,  $^{208}\text{Po}$ , 0.3 g  $\text{NaCl}$  and 20 mL aqua regia to 150 mL beaker. Digest for 90 min on a 250°C plate. Add 10 mL 14 M  $\text{HNO}_3$ . Digest for 1 h on a 250°C plate. Cool the sample for 15 min with water and dilute to 120 mL with water. Filter the sample through a glass fibre paper GF/F to a 250 mL plastic centrifuge tube. Wash the beaker and residue with 10 mL 1 M  $\text{HCl}$ . Discard the residue. Add  $\text{NH}_3$  to pH = 9, centrifuge and discard the supernatant. The precipitate is dissolved in 1 mL 12 M  $\text{HCl}$ . Transfer the sample to a glass tube. Wash the centrifuge tube with 30 mL 0.1 M  $\text{HCl}$  and combine to the glass tube. Goes to step 3).

(Petroleum Sample: Add 0.100-0.500 g petroleum (Stir to uniformity)  $^{208}\text{Po}$ , 30 mL 14 M  $\text{HNO}_3$ , 10 mL 12 M  $\text{HCl}$  and 0.3 g  $\text{NaCl}$  to 500 mL flask. Digest for 5 h on  $250^\circ\text{C}$  plate. Evaporate to dryness on  $120\text{-}130^\circ\text{C}$  plate. Add 20 mL aqua regia and condense for 1 h. on  $250^\circ\text{C}$  plate. Evaporate to dryness on a  $120\text{-}150^\circ\text{C}$  plate. Add 10 mL 30%  $\text{H}_2\text{O}_2$  (be careful the reaction is very strong) and evaporate to dryness on  $120^\circ\text{C}$  plate. Add 10 mL 12 M  $\text{HCl}$  and evaporate to dryness on  $120\text{-}150^\circ\text{C}$  plate. Go to step 2).

(Second polonium analysis for calculation of  $^{210}\text{Pb}$ : Transfer the storage solution to a 500 mL flask. Add 8 mL aqua regia to the container and cover the container with disc condensing for 30 min on  $150^\circ\text{C}$  plat. Transfer the aqua regia to the flask. Wash the container 2 times, each time with 2 mL 14  $\text{HNO}_3$  and transfer the solutions to the flask. Add  $^{208}\text{Po}$  to the flask. Evaporate the solution to dryness on a  $120^\circ\text{C}$  plate. Add 20 mL aqua regia to the flask and condense for 1 h on  $250^\circ\text{C}$  plate. Evaporate to dryness on a  $120^\circ\text{C}$  plate. Go to step 2).

2. Add 5 mL 30%  $\text{H}_2\text{O}_2$ . Digest for 10 min on a  $200^\circ\text{C}$  plate. Add 0.8 mL 12 M  $\text{HCl}$ . Digest for 10 min on a  $200^\circ\text{C}$  plate. Add 15 mL water. Digest for 15 min on a  $200^\circ\text{C}$  plate. Add 1 g  $\text{NH}_2\text{OH.HCl}$ . Digest for 10 min. on a  $200^\circ\text{C}$  plate. Cool the sample for 15 min with water. Filter the sample through a Munktell Analytical filter paper. Wash the residue and flask 3 times each time with 3 mL 0.3 M  $\text{HCl}$  containing 1 mg/mL  $\text{NaCl}$ . The acidity of the 30 mL of filtrate is 0.3-0.5 M  $\text{HCl}$ .
3. The clean silver disc is fixed in a special Teflon holder (figure-2, see Appendix -2.) which is suspended by a polyethylene thread in a vertical position in the solution exposing one side of the silver disc. Pure polonium metal is deposited on the silver disc surface by thermal decomposition at  $90^\circ\text{C}$  under magnetic stirring for 3 h.
4. Dip the holder with the silver disc in distilled water twice, each time for 2 seconds. Dismantle the silver disc from the holder and dip the disc into distilled water 2 times, each time for 2 seconds. The water on the disc surface is sucked in with soft paper. Put the disc in  $90^\circ\text{C}$  heating cabinet for 15 min and the sample is ready for  $\alpha$  - measurement.

#### Procedure for $^{210}\text{Pb}$

5. After thermal decomposition of polonium, add 2 mL 30% $\text{H}_2\text{O}_2$  and evaporate the solution to 5 mL on a  $150^\circ\text{C}$  plate. Transfer the sample to a 150 mL separator. Wash the beaker with 25 mL 12 M  $\text{HCl}$  and transfer to the separator to obtain a concentration of 10 M  $\text{HCl}$ . Extract with 30 mL 5% $\text{TIOA}$ /xylene. Shake 3 min. Wash the organic phase with 5 mL 10 M  $\text{HCl}$ . Shake 3 min. Combine the 2 aquatic phases to stand for  $^{210}\text{Po}$  ingrowth from  $^{210}\text{Pb}$ . Discard the organic phase, which contains  $\text{Po}$ ,  $\text{Fe}$ ,  $\text{U}$  and  $\text{Pu}$ .
6. After a suitable ingrowth period (about 6 months), add  $^{208}\text{Po}$  and stir to uniformity. Transfer the solution to a 500 mL flask. Add 8 mL aqua regia to the container cover the container with a disc. Condense for 30 min on a  $150^\circ\text{C}$  plate. Wash the container 2 times, each time with 3 mL 14  $\text{HNO}_3$ . Combine the solutions to the flask. Evaporate to dryness on a  $120^\circ\text{C}$  plate.

7. Add 20 mL aqua regia and condense for 1 h on a 250 oC plate. Evaporate to dryness on a 120oC plate.
8. Repeat the steps 2, 3, 4.
9. According to the ingrown time and second polonium activity to calculate the  $^{210}\text{Pb}$  activity. (See appendix –1)

## References

1. Qingjiang Chen et al, Determination of plutonium in environmental samples by controlled valence in anion exchange, Journal of Radioanalytical and Nuclear Chemistry, Vol. 1723 No. 2(1993) 281-288.
2. R.J.H. Clark, Vanadium, Comprehensive Inorganic Chemistry, Vol. 3, p-519.
3. Chen Qingjiang et al. A rapid separation of  $^{210}\text{Po}$  from  $^{210}\text{Pb}$  by TIOA extraction, NUK, Risø National Laboratory, Denmark(unpublished)

## Appendix-1

Table 1. Ingrowth of Po-210 from 100 Bq Pb-210.

Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)	Day	Po-210 (Bq)
1	0.03	51	19.59	101	37.27	151	50.94	201	61.49	251	69.61	301	75.85	351	80.61
2	0.12	52	19.99	102	37.58	152	51.18	202	61.67	252	69.75	302	75.95	352	80.69
3	0.27	53	20.39	103	37.89	153	51.41	203	61.86	253	69.90	303	76.06	353	80.77
4	0.46	54	20.78	104	38.19	154	51.65	204	62.04	254	70.04	304	76.17	354	80.86
5	0.69	55	21.18	105	38.50	155	51.89	205	62.22	255	70.17	305	76.28	355	80.94
6	0.95	56	21.57	106	38.80	156	52.12	206	62.40	256	70.31	306	76.38	356	81.02
7	1.24	57	21.96	107	39.10	157	52.35	207	62.58	257	70.45	307	76.49	357	81.10
8	1.56	58	22.35	108	39.40	158	52.59	208	62.76	258	70.59	308	76.59	358	81.18
9	1.89	59	22.73	109	39.70	159	52.82	209	62.94	259	70.72	309	76.70	359	81.26
10	2.25	60	23.12	110	40.00	160	53.05	210	63.11	260	70.86	310	76.80	360	81.34
11	2.62	61	23.50	111	40.29	161	53.27	211	63.29	261	71.00	311	76.90	361	81.42
12	3.00	62	23.88	112	40.59	162	53.50	212	63.46	262	71.13	312	77.01	362	81.49
13	3.40	63	24.26	113	40.88	163	53.73	213	63.64	263	71.26	313	77.11	363	81.57
14	3.81	64	24.63	114	41.17	164	53.95	214	63.81	264	71.40	314	77.21	364	81.65
15	4.22	65	25.01	115	41.46	165	54.17	215	63.98	265	71.53	315	77.31	365	81.73
16	4.64	66	25.38	116	41.75	166	54.40	216	64.15	266	71.66	316	77.41	366	81.80
17	5.06	67	25.75	117	42.03	167	54.62	217	64.32	267	71.79	317	77.51	367	81.88
18	5.49	68	26.12	118	42.32	168	54.84	218	64.49	268	71.92	318	77.61	368	81.95
19	5.92	69	26.48	119	42.60	169	55.06	219	64.66	269	72.05	319	77.71	369	82.03
20	6.36	70	26.85	120	42.88	170	55.27	220	64.83	270	72.18	320	77.81	370	82.10
21	6.80	71	27.21	121	43.16	171	55.49	221	65.00	271	72.31	321	77.91	371	82.18
22	7.24	72	27.57	122	43.44	172	55.71	222	65.16	272	72.43	322	78.01	372	82.25
23	7.68	73	27.93	123	43.72	173	55.92	223	65.33	273	72.56	323	78.10	373	82.33
24	8.12	74	28.29	124	44.00	174	56.13	224	65.49	274	72.69	324	78.20	374	82.40
25	8.56	75	28.64	125	44.27	175	56.35	225	65.66	275	72.81	325	78.29	375	82.47
26	9.00	76	29.00	126	44.54	176	56.56	226	65.82	276	72.94	326	78.39	376	82.54
27	9.44	77	29.35	127	44.82	177	56.77	227	65.98	277	73.06	327	78.48	377	82.62
28	9.88	78	29.70	128	45.09	178	56.98	228	66.14	278	73.18	328	78.58	378	82.69
29	10.32	79	30.05	129	45.36	179	57.18	229	66.30	279	73.31	329	78.67	379	82.76
30	10.76	80	30.39	130	45.62	180	57.39	230	66.46	280	73.43	330	78.77	380	82.83
31	11.20	81	30.74	131	45.89	181	57.59	231	66.62	281	73.55	331	78.86	381	82.90
32	11.64	82	31.08	132	46.15	182	57.80	232	66.77	282	73.67	332	78.95	382	82.97
33	12.07	83	31.42	133	46.42	183	58.00	233	66.93	283	73.79	333	79.04	383	83.04
34	12.50	84	31.76	134	46.68	184	58.21	234	67.09	284	73.91	334	79.13	384	83.11
35	12.94	85	32.10	135	46.94	185	58.41	235	67.24	285	74.03	335	79.22	385	83.18
36	13.37	86	32.43	136	47.20	186	58.61	236	67.40	286	74.15	336	79.31	386	83.25
37	13.79	87	32.77	137	47.46	187	58.81	237	67.55	287	74.27	337	79.40	387	83.31
38	14.22	88	33.10	138	47.72	188	59.00	238	67.70	288	74.38	338	79.49	388	83.38
39	14.65	89	33.43	139	47.97	189	59.20	239	67.85	289	74.50	339	79.58	389	83.45
40	15.07	90	33.76	140	48.23	190	59.40	240	68.00	290	74.61	340	79.67	390	83.51
41	15.49	91	34.09	141	48.48	191	59.59	241	68.15	291	74.73	341	79.76	391	83.58
42	15.91	92	34.41	142	48.73	192	59.79	242	68.30	292	74.84	342	79.84	392	83.65
43	16.33	93	34.74	143	48.98	193	59.98	243	68.45	293	74.96	343	79.93	393	83.71
44	16.74	94	35.06	144	49.23	194	60.17	244	68.60	294	75.07	344	80.02	394	83.78
45	17.15	95	35.38	145	49.48	195	60.36	245	68.75	295	75.18	345	80.10	395	83.84
46	17.57	96	35.70	146	49.72	196	60.55	246	68.89	296	75.30	346	80.19	396	83.91
47	17.97	97	36.02	147	49.97	197	60.74	247	69.04	297	75.41	347	80.27	397	83.97
48	18.38	98	36.33	148	50.21	198	60.93	248	69.18	298	75.52	348	80.36	398	84.04
49	18.79	99	36.65	149	50.46	199	61.12	249	69.33	299	75.63	349	80.44	399	84.10
50	19.19	100	36.96	150	50.70	200	61.30	250	69.47	300	75.74	350	80.53	400	84.16



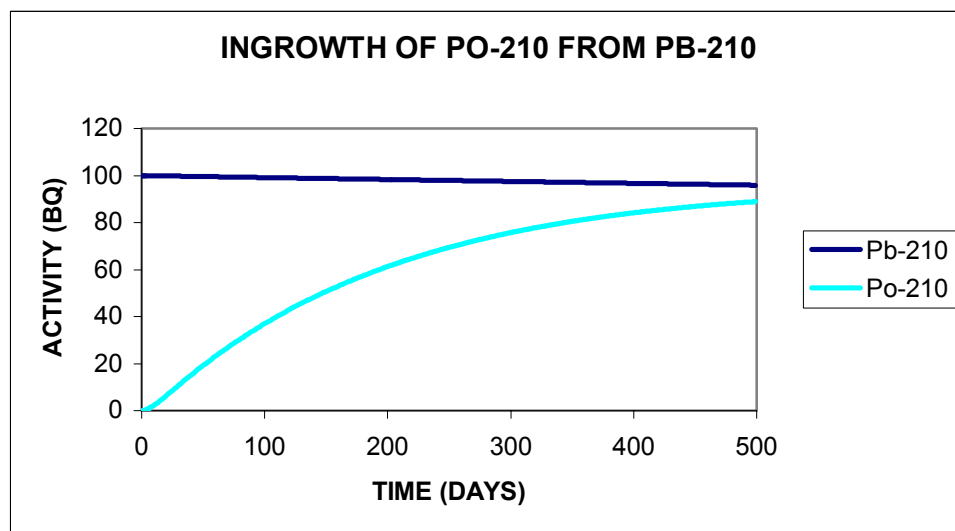
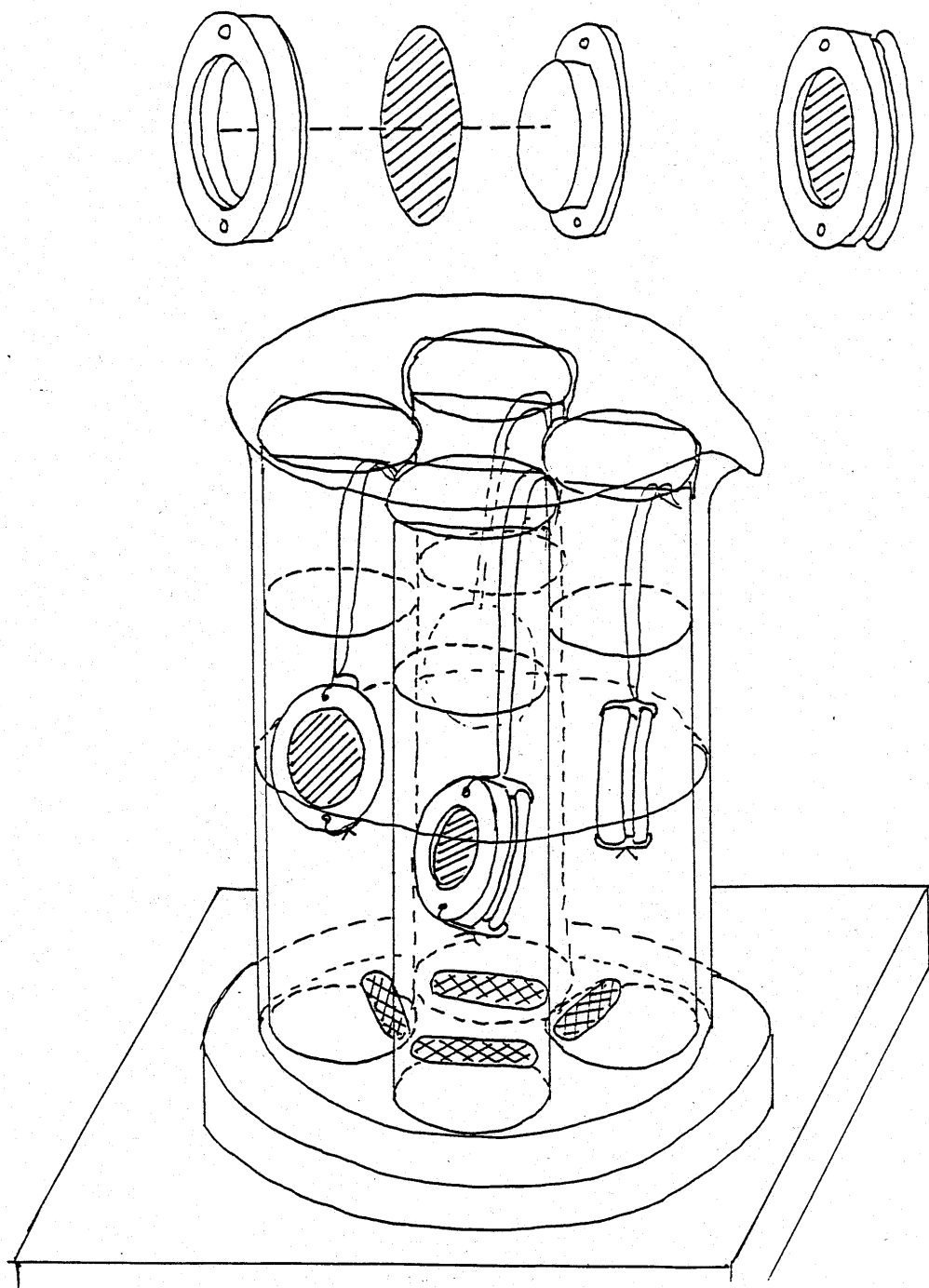


Fig. 1. Ingrowth of Po-210 from 100 Bq Pb-210.

The ingrowth of Po-210 shown in Table 1 and in Fig. 1 is calculated from an initial pure Pb-210 activity of 100 Bq. The following half-lives were used: 22.3 y for Pb-210, 5.012 d for Bi-210 and 138.38 d for Po-210.



Appendix-2,  
Figure 4. Teflon Holder suspended by a polyethylene thread in a vertical position in solution, exposing one side of the silver disc, under magnetic stirring at 90 °C.

13

## Title and authors

Procedures for Determination of  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{237}\text{Np}$ ,  $^{234,238}\text{U}$ ,  $^{228,230,232}\text{Th}$ ,  $^{99}\text{Tc}$  and  $^{210}\text{Pb} - ^{210}\text{Po}$  in Environmental Materials

Qingjiang Chen, Asker Aarkrog, Sven P. Nielsen, Henning Dahlgaard, Bjørn Lind, A.K. Kolstad and Yixuan Yu

ISBN

ISSN

87-550-2871-3; 87-550-2966-3(Internet)

0106-2840

Department or group

Date

Nuclear Safety Research

2001-12-07

Groups own reg. number(s)

Project/contract No(s)

Sponsorship

Pages

Tables

Illustrations

References

33

1

2

3

Abstract (max. 2000 characters)

Since 1987, the Department of Nuclear Safety Research, Risø National Laboratory has developed procedures for analysis of low-level amounts of radioactivity in large samples of 200 liters seawater, 10 gram sediment, soil and other environmental materials. These analytical procedures provide high chemical yields, good resolution and excellent decontamination factors for large environmental samples analysed by alpha spectrometry and mass spectrometry (ICPMS). The procedures have been checked through practical analysis work and are used in Norway, the Netherlands, Germany, Spain, France and Denmark.

Descriptors

Determination, Procedures, Pu, Am, Np, U, Th, Tc, Pb, Po, large environmental sample, alpha-spectrometry, ICPMS

Available on request from Information Service Department, Risø National Laboratory,  
(Afdelingen for Informationsservice, Forskningscenter Risø), P.O.Box 49, DK-4000 Roskilde, Denmark.  
Telephone +45 4677 4004, Telefax +45 4677 4013